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Branching ratio for the $^5S^o_2$ - $^3P_{2,1}$ inter-system resonance multiplet in P II

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Abstract. The P II inter-system multiplet, $3s3p^3\ ^5S^o_2\ -\ 3s^23p^2\ ^3P_{2,1}$ at λ_{air} = 221.033nm and 219.556nm, have been observed in emission from a low-pressure inductively-coupled plasma source. The measured branching ratio, A_{2210}/A_{2196} = 3.04 ± 0.15, is in agreement with recent *ab initio* calculations. Absolute transition probabilities, A_{2210} = 4500 ± 330 s^{-1} and A_{2196} = 1480 ± 120 s^{-1}, are determined by combining the measured branching ratio with the previously measured lifetime of the $^5S^o_2$ metastable level.

Key words: atomic data – methods: laboratory

1. Introduction

Weak inter-system lines in low atomic number atoms and ions have received considerable attention in recent years. Inter-system refers to lines that arise from transitions between different multiplet systems so that the selection rule $\Delta S = 0$ is violated. In the limit of pure LS-coupling, such transitions are forbidden to all orders. In practice, an electric-dipole transition probability is present because of non-negligible spin-orbit interactions which mix levels of different spin. This mixing is extremely small in low-lying levels of the He atom, but slowly increases in strength with increasing atomic number (and rapidly with charge-state in an iso-electronic sequence) so that for very heavy atoms (or high charge-state ions) these lines can be very strong. One example is the resonance line of Hg I at 253.7nm ($6^3P^o_1$ - 6^1S_0).

It is the appearance of very weak inter-system lines in the lighter elements which has attracted so much attention from atomic theorists because the strength of such lines is a sensitive indicator of small deviations from the LS-coupling scheme. For this reason, the associated branching fractions, lifetimes, energy levels, and fine-structure splitting serve as challenging tests for different theoretical approximations (Ellis 1989, Martinson and Ellis 1985). Accurate experimental data are needed for these tests.

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Weak inter-system lines are also used as diagnostics of astrophysical plasmas (Smith et al. 1984a) and have been observed in many astrophysical sources (See for example *The Universe at Ultraviolet Wavelengths* 1981 or *Advances in Ultraviolet Astronomy* 1982). The long-lived nature of the upper level makes the observed intensity ratio of an inter-system line to an allowed line sensitive to the collisionality of the local environment, so that the inter-system line can be used as a probe of electron density and temperature. The weak oscillator strengths of these lines makes them useful for measurements of column densities in the interstellar medium because such transitions are not easily saturated (Hobbs et al. 1982, Cowan et al. 1982). Again, accurate experimental measurements are needed for these applications.

Unfortunately, the properties that make weak inter-system lines useful in astrophysical sources, also make them very difficult to observe in the laboratory (Edlen et al. 1969). Radiative decay is so slow that collisional quenching of the excited state usually dominates. Consequently, these lines are often seen only very weakly or not at all, in the laboratory, and many of the sought-after parameters have not been measured, to any accuracy. Even when experimental data exist, discrepancies often persist. Such a situation has been noted in the CI-like iso-electronic sequence (Brage 1997).

We present measurements of the branching ratio for the $3s3p^3\ ^5S^o_2\ -\ 3s^23p^2\ ^3P_{2,1}$ inter-system multiplet in singly-ionized phosphorus, at λ_{air} = 221.033nm and 219.556nm, respectively (Martin et al. 1985). The branching ratio is combined with the previously measured lifetime of the $^5S^o_2$ level (Calamai et al. 1992) to obtain the first experimentally determined transition probabilities for this inter-system pair. This ratio, as well as data for the rest of the Si I iso-electronic sequence, has been the subject of several recent theoretical studies (Fritzche and Grant 1994, LaJohn and Luke 1993a&b, Hibbert 1993, Brage et al. 1993, Brage and Fischer 1993, Hibbert 1988, Ellis and Martinson 1984). Some pertinent data for P II are listed in Table 1.

2. Experiment

The spectroscopic source of P II is a low-pressure ICP (inductively-coupled plasma). This type of source has been

Table 1. Some calculated and experimental data for the $^5S_2^o - ^3P_{2,1}$ transitions in PII. (The last line of data is produced by combining the present results with the $^5S_2^o$ lifetime measured by Calamai.)

	$A_{2211}(s^{-1})$	$A_{2196}(s^{-1})$	$\tau(\mu s)$ $^5S_2^o$	Branching ratio
Calculations				
Ellis and Martinson(1984)	1420	508	519	2.80
Huang (1985)	2972	699	272	4.25
Hibbert(1993)	-	-	163	-
Brage, Merkelis, and Fischer (1993)	3692	1255	202	2.94
LaJohn and Luke (1993a)	4160	1460	178	2.85
Fritzshe and Grant (1994)	1299 - 21293	614 - 6832	35.6 - 523	2.12 - 3.12
Brage (1997)	3681 - 4337	1252 - 1509	172 - 203	2.82 - 2.94
Experiment				
Calamai (1992)			167 ± 12	
Present results				$3.04 \pm .15$
combined	4500 ± 330	1480 ± 120		

widely used for observing singly-ionized spectra (Curry et al. 1997, Svendinius et al. 1983, Svendenius 1980) because it can be operated at high input powers and low neutral pressures. Such a combination produces a large and strongly excited ion population. Also important for the present work is the absence of electrodes in contact with the plasma. Electrodes are a potential source of impurity lines and may initiate unwanted chemistry with phosphorus radicals.

The ICP consists of a specially designed fused-silica cell and a cylindrical six-turn RF coil. The coil is driven at 13.56 MHz by a high-power radio-frequency source through a capacitive matching network. The cylindrical fused-silica cell is 2 inches in diameter and 4 inches long, with a long, small diameter tube attached to each end. The small diameter of the tubes act as an effective trap for evaporated phosphorus, condensing the vapor before it diffuses to other parts of the vacuum system. No other traps are necessary.

Closed cells with relatively small neutral fill pressures rapidly become contaminated under high power operation and re-ignition of a discharge becomes impossible. Even without impurities, it is often only possible to initiate a discharge with a higher fill pressure or with a different fill gas than is to be used during the experiment. It is vital to have a flowing-gas cell to limit the build-up of impurities in the discharge and to facilitate ignition of the discharge.

Both a pure He and a He-Ar mixture have been used during discharge operation, at pressures between 50 and 100 mTorr. P_4 is introduced by placing a lump of red phosphorus at a judicious location near the edge of the discharge, so that the plasma provides the heat to produce evaporation. The vapor pressure of the P_4 molecule is 10^{-4} Torr at 130°C and 10^{-3} Torr at 160°C (*The Characterization of High-Temperature Vapors* 1967). By using a fill gas to sustain the discharge, the RF coupling is insensitive to the presence of small amounts of an additive gas, so the P_4 vapor pressure can be controlled with the RF input power.

Helium is chosen as the primary fill gas for this experiment because of its very large excitation energy. The lowest excited state is the 2^3S metastable level at 19.8 eV above the ground state. Excited He atoms and He ions dissociate phosphorus molecules and ionize monoatomic phosphorus. The dissociation energy of P_4 into P_2 is 2.4eV(*Thermodynamic Properties of the Elements* 1956), and the dissociation energy of P_2 is 5.0eV (Huber and Herzberg 1979). The ionization energy of monoatomic phosphorus 11.0 eV. A higher electron temperature is also obtained with He than with other rare gases (Schwabedissen et al. 1997), leading to thorough fragmentation of phosphorus molecules and substantial excitation of electronic energy levels. All of these factors are favorable for maximizing P II emission relative to molecular and neutral atomic emission (Svendenius 1980).

The lines of interest are observed with a 0.5-meter Ebert-Fastie spectrometer equipped with a 316 grooves/mm echelle grating. Both the 221.0nm and 219.6nm lines are observed simultaneously in 26^{th} order using a photo-diode array. A 0.1-meter Seya-Namioka pre-mono-chromator is proximity-coupled to the Ebert-Fastie spectrometer to eliminate overlapping orders of the echelle grating. A radiometric calibration to correct for the pre-monochromator bandpass function, pixel-to-pixel variations in sensitivity of the photo-diode array, and residual vignetting effects occurring in the Ebert-Fastie spectrometer is determined with a deuterium lamp, in conjunction with a fused-silica optical diffuser.

A small amount of Ar is added to the discharge to facilitate low power operation. When operating the source at high RF input powers, and therefore high P_4 densities, a molecular band from another echelle order appears in the region surrounding the 219.6nm line. The high threshold for H-mode operation of a pure He discharge prevents the source from being operated at lower powers (Schwabedissen et al. 1997, Kortshagen et al. 1996). Changing the buffer gas mix is more convenient than breaking vacuum and trying to move the solid phosphorus just

a little farther from the discharge in order to reduce evaporation. A small amount of Ar (1-20 mTorr) is added to lower the H-mode threshold. Operating at lower input powers lowers the wall temperature of the discharge and the P_4 density sufficiently to suppress the interferring molecular band.

There has been no effort to measure the phosphorus vapor pressure directly, but from changes in the RF coupling it is estimated that it can be no higher than 5 mTorr, and is quite likely less than 1 mTorr in all cases. The temperature on the outside of the fused-silica cell at the location of the red phosphorus is measured with a thermocouple, isolated from the ambient by several layers of insulating tape. The measured temperatures do not exceed 160°C for any of the measurements, although the discharge can easily be run much hotter than this.

3. Discussion

A typical P II emission spectrum, acquired with 0.006nm full-width half-maximum spectral resolution, is shown in Figure 1. The measured intensity ratio of the $^5S^o_2 - {}^3P_2$ transtion at 221.0nm to the $^5S^o_2 - {}^3P_1$ transition at 219.6nm is A_{2210}/A_{2196} = 3.04 ± 0.15. Because the two lines can be observed simultaneously, there are no errors due to drifts of the source. Therefore, long integration times can be used to reduce photon statistical noise. Depending upon source conditions, integration times range from 1 to 10 minutes, resulting in statistical uncertainties in the final measurement of less than 2%. The spectrum shown in Figure 1 has already been divided by the radiometric curve obtained with the deuterium lamp, and so exhibits the true signal-to-noise arising from both the measurement and the radiometric correction.

Although the echelle grating gives greatly improved dispersion and resolution over a standard grating, it has the difficulty that many spectral orders overlap.

Unwanted orders can be very effectively eliminated with the use of a pre-monochromator with a suitably narrow bandpass, such as the Seya-Namioka instrument used here. However, when extremely weak lines are being observed, as in the present case, a small amount of leakage from other orders can sometimes be observed. In Figure 1, an off-order Ar line can be seen on the short wavelength side of the 219.6nm line. The relative intensity of the Ar line is only about 10% and it is almost completely resolved from the 219.6nm line. The two lines are separated by 0.012nm and the spectral resolution is 0.006nm. The line appearing at 220.7nm is actually a He I line at 318.77nm in 18^{th} order.

Possible systematic effects at the 5% level and below are difficult to identify. We can say, however, that because of the small transition probabilities of these lines it is certain that radiation trapping does not occur. In addition, both lines originate from a common upper level, so collisional processes do not influence their relative intensities. A check for errors in the radiometric correction is made by changing the position of the lines relative to the pre-monochromator bandpass and to the photodiode array, independently. Although we have used a resolving power of 35,000, there is also the possibility of a weak unresolved blend.

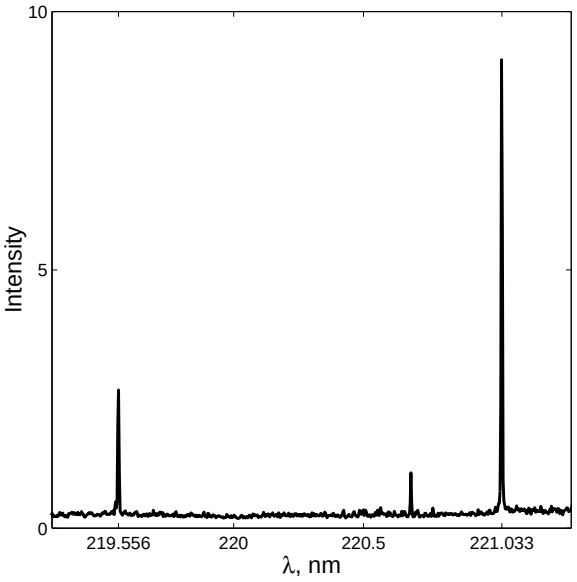

Fig. 1. P II spectrum showing the $^5S^o_2 - {}^3P_2$ branch at 221.033nm and the $^5S^o_2 - {}^3P_1$ branch at 219.556nm. The spectral resolution is .006nm.

Difficulties in calculating parameters such as branching ratios, fine-structure splitting, and lifetimes for weak inter-system lines have been noted (Brage 1997, Ellis 1989, Martinson and Ellis 1985). Several calculations of the $^5S^o_2 - {}^3P_{2,1}$ multiplet branching ratio in P II have been presented in recent years which have varied by as much as a factor of two (see Table 1), although most are in the range 2.81-2.94. Many of the efforts have focussed on the lifetime of the $^5S^o_2$ level which was measured by Calamai (1992). However, Brage (1997) has shown that the lifetime and branching ratio are influenced by different physical effects.

Recent *ab initio* calculations by Brage (1997) have given a ratio in the range 2.82-2.94 depending on the number of terms mixing with the $^5S^o_2$ level and the exact form of the Hamiltonian used. The present measurement confirms the upper end of this range, although the experimental uncertainty is not yet small enough to differentiate between some of the theoretical fine-tuning that has been attempted recently.

No precise measurements for this branching ratio have been made previously. An early laboratory observation by Martin (1959) yielded an estimated ratio of 2.5, with no experimental uncertainty given. Svendinius (1983) observed a ratio of 0.5, but this anomalous result was later shown to be caused by a contaminating P IV line (Smith et al. 1984b). A measurement of the same ratio in iso-electronic S III (the branching ratio is expected to vary slowly along an iso-electronuc sequence) yielded a value of 2.7 (Moos et al. 1983). This latter result is in agreement with Brage's (1997) calculations for S III.

The P II 219.6nm and 221.0nm lines are the only significant decay branches of the $^5S^o_2$ metastable level, so absolute transition probabilities for these transitions can be obtained by combining our measured branching ratio with the previously

measured lifetime of the $^5S_2^o$ level (Calamai et al. 1992). Using $\tau = 167 \pm 12\mu$sec, the absolute transition probabilities are $A_{2210} = 4500 \pm 330$ s^{-1} and $A_{2196} = 1480 \pm 120$ s^{-1}.

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